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LAMINATE CERAMIC CONDENSER AND MANUFACTURING METHOD THEREOF
[Sekisou seramiku kondensa to sono seizou houhou]

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Claims

1. For a laminate ceramic condenser for which internal electrodes formed by means of conductors that oppose [one another] with an inductive ceramic layer intervening, a laminate ceramic condenser characterized in that the inductive ceramic and the internal electrodes are baked in a reduced oxygen atmosphere.
2. For a manufacturing method whereby an electroconductive paste containing Ag or an Ag alloy is applied to unbaked inductive ceramic sheets and these ceramic sheets are layered and baked to form a laminate ceramic condenser for which internal electrodes formed by means of conductors that oppose [one another] with an inductive ceramic layer intervening, a laminate ceramic condenser manufacturing method characterized in that the baking atmosphere is made a reduced oxygen atmosphere.
3. For a manufacturing method whereby a ceramic paste and an electroconductive paste containing Ag or an Ag alloy are alternately applied and the obtained laminate is baked to form a laminate ceramic condenser with internal electrodes formed by means of conductors that oppose [one another] with an inductive ceramic layer intervening, a laminate ceramic condenser manufacturing method characterized in that the baking atmosphere is a reduced oxygen atmosphere.
4. A method for manufacturing a laminate ceramic condenser characterized in that the reduced oxygen atmosphere recorded in the aforementioned second or third claim has an oxygen density of 50,000 ppm or less.

Detailed explanation of the invention

Industrial application field

The present invention pertains to a laminate ceramic condenser wherein Ag or Ag-Pd conductors are made the internal electrodes and to a manufacturing method thereof.

Prior art

With the increased miniaturization and high densification of electronic components, attention has focused on [the use of] laminate ceramic condensers as condensers that are able to obtain a large electrostatic capacity while remaining small in size. Furthermore, with the increased use of these laminate ceramic condensers the demand for a reduction in the manufacturing cost has increased, and to meet this demand various techniques have been developed. As a representative example, an inductive ceramic material capable of low-temperature sintering has been developed, so the baking cost has been reduced, and the paste material used to print and form internal and external electrodes can be baked at a relatively low temperature, [so the condenser] can be formed of a paste that has a low-cost metal as its principal component. In this way, the manufacturing cost can be lowered while maintaining the characteristics required for a ceramic condenser, resulting in reduced costs.

A laminate ceramic condenser is [formed by] printing an electroconductive paste in a square on unbaked ceramic sheets, then stacking [said sheets] such that the patterns of the aforementioned electroconductive paste are shifted from one another. Subsequently it is cut into the shape of a chip such that the aforementioned electroconductive paste patterns are exposed at the opposing ends. The laminate chips thus formed are introduced into a furnace and baked; after which external electrodes are formed at the opposing ends of said chips for example by applying an electroconductive paste, baking it, and plating it. In this way, a laminate ceramic condenser is formed.

Figure 1 illustrates the configuration of a laminate ceramic condenser thus formed: 5 are inductors formed by sintering the aforementioned ceramic sheets; 6 are electrodes that oppose one another and are sandwiched between said inductors; and 3 are external electrodes that are formed along opposite ends and the upper, lower and side surfaces of the laminate such that they are electrically connected to these electrodes 6, 6 respectively.

Conventionally [a material] primarily having Pd as the conductor has been used as the material, that is the electroconductive paste used to print and form the aforementioned internal electrodes 6, 6 of the laminate ceramic condenser; however, by using an electroconductive paste having an Ag-Pd alloy that contains Ag as the conductor and by using [a material] that can be baked at a relatively low temperature as the inductive ceramic material, a cost reduction can be achieved.

Problem to be solved by the invention

However, in practice the following problems exist.

First, when the cost of the electroconductive paste is considered, the market price of Pd is approximately 10 times that of Ag, so when the percentage of Ag is small a cost benefit is not obtained; in practice, a cost benefit is realized only when the percentage of Ag is 50% or more. Moreover, when the electrical resistance of the conductor is considered, when the amount of Ag is 50% or more by weight, the electrical resistance of an internal electrode that is formed decreases as the amount of Ag increases. Specifically, if the amount of Ag is less 70% the electrical resistance of the internal electrode is high and the high-frequency characteristic of the laminate condenser is poor, which is not practical.

On the other hand, [when] Ag or an Ag-Pd alloy for which Ag is 70% or more by weight is [used] as the conductor used for the electroconductive paste, its melting point and its solidus temperature is low. The melting point of Ag is 960°C, and for an Ag-Pd alloy – for example, one for which the percentage Ag is 80% or more by weight – the solidus temperature is 1070°C.

When a laminate condenser chip is baked and the electroconductive paste used to form the internal electrodes is baked at a temperature close to the melting point or the solidus temperature of the conductive material, the conductive material diffuses into the inductive ceramic, reducing the insulating property of the inductive ceramic and decreasing the reliability of the condenser. Accordingly, with the

prior art, to eliminate this problem the laminate is baked at a temperature that is approximately 100°C less than the melting point or the solidus temperature of the aforementioned conductive material; in practice, when an Ag-Pd alloy paste with the percentage of Ag in the alloy 80% by weight is used, the laminate is baked at a temperature of approximately 970°C.

However, to bake the laminate at a low temperature an inductive ceramic material that can be baked at a low temperature must be used; therefore, for example, the powder of the ceramic source material must be finely pulverized, and a means to add a large amount of an agent that promotes sintering to the material must be used. However, there is a disadvantage in that an inductive ceramic material that uses a finely powdered source material costs much, which increases the cost of the laminate condenser; in addition, when a large amount of an agent that promotes sintering is added there is a disadvantage in that it decreases the specific inductivity of the inductive ceramic and the product quality coefficient (Q) of the condenser.

Furthermore, there is a problem in that even when the laminate is baked at the aforementioned low temperature of approximately 970°C, the diffusion of the conductor into the inductive ceramic cannot be prevented completely, so a deterioration in the characteristics of the condenser cannot be prevented.

Accordingly, the purpose of the present invention is to offer a laminate ceramic condenser and a manufacturing method thereof that can eliminate the aforementioned problems.

Means to solve the problem

In other words, the gist of the means to achieve the aforementioned problem is, first, for a laminate ceramic condenser for which internal electrodes formed by means of conductors that oppose [one another] with an inductive ceramic layer intervening, a laminate ceramic condenser characterized in that the inductive ceramic and the internal electrodes are baked in a reduced oxygen atmosphere.

Secondly, for a manufacturing method whereby an electroconductive paste containing Ag or an Ag alloy is applied to unbaked inductive ceramic sheets and these ceramic sheets are layered and baked to form a laminate ceramic condenser for which internal electrodes formed by means of conductors that oppose [one another] with an inductive ceramic layer intervening, a laminate ceramic condenser manufacturing method characterized in that the baking atmosphere is a reduced oxygen atmosphere.

Thirdly, for a manufacturing method whereby a ceramic paste and an electroconductive paste containing Ag or an Ag alloy are alternately applied and the obtained laminate is baked to form a laminate ceramic condenser for which internal electrodes formed by means of conductors that oppose [one another] with an inductive ceramic layer intervening, a laminate ceramic condenser manufacturing method characterized in that the baking atmosphere is a reduced oxygen atmosphere.

Moreover, in practice the aforementioned reduced oxygen atmosphere is an atmosphere with an oxygen density of 50,000 ppm or less.

Operation

When Ag or an electroconductive paste containing Ag is baked in an atmosphere with an oxygen density sufficiently lower than that of normal atmosphere - specifically, an atmosphere with an oxygen density of 50,000 ppm or less – the activity of the Ag is reduced, and during baking the degree of diffusion of the AG into the ceramic can be significantly suppressed. Consequently, even when baking occurs at a temperature that is close to the melting point of the Ag or to the solidus temperature of an Ag alloy; it is difficult for the Ag to diffuse into the ceramic substrate. Accordingly, the insulation resistance of the ceramic is not reduced. Therefore, when using an electroconductive paste that includes a greater percentage of Ag than with the prior art the inductive ceramic the electroconductive paste can be baked at a temperature that is higher than that of the prior art.

Application Examples

Next, practical application examples of the present invention will be explained in detail.

Application Example 1

A ceramic powder consisting respectively of 97% TiO_2 , 2% CuO , and 1% ZrO_2 by weight, an organic binder of a polyvinyl-butyl in a 1-1 solvent mixture of toluene and ethanol, di-butyl phthalate (plasticizer), and oleic acid (dispersant) were mixed in a ball mill to prepare a slurry of a ceramic material.

This slurry was defoamed in a vacuum defoamer, after which a 40 μm thick length of green sheet was formed using a doctor plate method. This green sheet was cut to a specified size; for example, 150 mm X 120 mm, and a commercially available Ag-Pd paste (solidus temperature approximately 1070°C) with the aforementioned Ag: Pd weight ratio being 8:2 was screen printed on this green sheet. A number of these sheets were stacked such that the patterns of the aforementioned electroconductive paste were shifted from one another, then [said sheets] were heat pressed with a pressure of 400 kg/cm^2 and a constant temperature of 100°C. This unbaked ceramic substrate was cut into the shape of chips such that one end of the aforementioned internal electrodes formed by the conductive paste was exposed at one end of the laminate and [one end was exposed] at the other.

First, this was heated at atmosphere from room temperature to 500°C at a temperature gradient of 1.5°C/min, then kept at 500°C for 2 h, then cooled to cooled to room temperature at a temperature gradient of -3°C/min to release the binder.

Next, nitrogen gas was introduced into a furnace, and after this had replaced the gas in the furnace the temperature was raised from room temperature to 1050°C at a temperature gradient of 5°C/min. The

temperature was kept at 1050°C for 1 h, then cooled to room temperature at a temperature gradient of – 5°C/min. At this time, the oxygen density in the furnace was measured by means of a Zirukoniya [transliteration] oxygen densitometer and found to be 10 ppm.

After baking, an electroconductive paste with Ag as the principal component was applied to the opposite ends of the aforementioned laminate chip and to the upper, lower and side surfaces connecting thereto; then this was baked at a temperature of 600°C to form the external electrodes. Then, nickel plating and solder plating was applied to these external electrodes.

The insulation resistance of 20 of the laminate ceramic condensers thus formed was measured at 100V DC; the resulting average value was $3.5 \times 10^{12} \Omega$. The results are shown in row E1 of the table below.

Application Examples 2-6

Laminate ceramic condensers were manufactured under the same conditions as in Application Example 1 except that the furnace atmosphere of the aforementioned Application Example 1 during baking was a nitrogen and air mixture with ratios of 2500:1, 500:1, 100:1, 20:1, and 3.2:1. The oxygen densities in the furnace for these cases are shown in rows E2-E6, respectively.

The insulation resistance of 20 each of the laminate ceramic condensers thus manufactured was measured, and the average values are shown in rows E2-E6.

Application Example 7

Laminate ceramic condensers were manufactured under the same conditions as in Application Example 1 except that the composition of the ceramic material powder was 95% TiO₂, 4% CuO, and 1%

ZrO₂, the electroconductive paste was an Ag paste, and the baking temperature was 940°C instead of 1050°C. The oxygen density in the furnace for this case is shown in row E7.

The insulation resistance of 20 of the laminate ceramic condensers thus manufactured was measured, and the average value is shown in row E7.

Comparative Examples 1,2

Various laminate ceramic condensers were manufactured under the same conditions as in Application Example 1, with a nitrogen and gas ratio of 1:1 as the furnace atmosphere during baking for the aforementioned Application Example 1, and with the furnace atmosphere during baking entirely air.

The insulation resistance of 20 each of the laminate ceramic condensers thus manufactured was measured, and the average values are shown in rows P1-P2.

Comparative Example 3

Laminate ceramic condensers were manufactured under the same conditions as in Application Example 7 except that the furnace atmosphere during baking was entirely air rather than nitrogen gas.

The insulation resistance of 20 each of the laminate ceramic condensers thus manufactured was measured, and the average value is shown in row P3.

No	(b) 内部 電極 Ag	(c) 焼成 温度 ℃	(a) 表 (d) 焼成 雰囲気 N ₂ /Air	(e) 酸素 濃度 ppm	(f) 直抵 流抗 Ω
E1	80%	1050	全 N ₂	10	3.5×10 ¹⁰
E2	80%	1050	2500	90	5.8×10 ¹⁰
E3	80%	1050	500	420	6.5×10 ¹⁰
E4	80%	1050	100	2100	5.2×10 ¹⁰
E5	80%	1050	20	10000	3.2×10 ¹⁰
E6	80%	1050	3.2	50000	1.0×10 ¹⁰
E7	100%	940	(g) 全 N ₂	10	2.5×10 ¹⁰
P1	80%	1050	1	105000	1.4×10 ⁶
P2	80%	1050	0	210000	8.0×10 ⁶
P3	100%	940	0	210000	1.2×10 ⁷

- Key: a Table
- b Internal electrode Ag
- c Baking temperature °C
- d Baking atmosphere N₂/Air
- e Oxygen density ppm
- f Insulation resistance Ω
- g All

Figure 2 is a graph indicating the relationship between the oxygen density of the atmosphere when baking a laminate chip and the average, maximum and minimum values of the insulation resistance of the laminate ceramic condensers based on the results of the aforementioned application examples and comparative examples.

Effect of the Invention

As explained in the above, by means of the present invention a laminate ceramic condenser with Ag or an Ag alloy as the conductor can be baked at a temperature that is higher than that of the prior art without decreasing its insulation resistance. Consequently, the effect that is achieved is that a highly reliable laminate ceramic condenser can be offered at a low price while preserving the characteristics required for a ceramic condenser.

Brief description of the figures

Figure 1 is an oblique schematic cross section illustrating one example of a laminate ceramic condenser.

Figure 2 is a graph indicating the relationship between the oxygen density of the atmosphere when baking a laminate chip and the average, maximum and minimum values of the insulation resistance of the laminate ceramic condensers.

Explanation of the reference numerals

- 3 External electrode
- 5 Inductor
- 6 Internal electrode

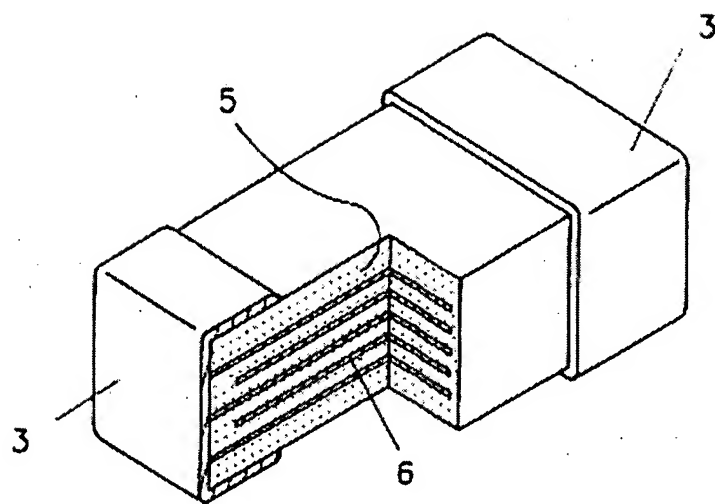


Figure 1

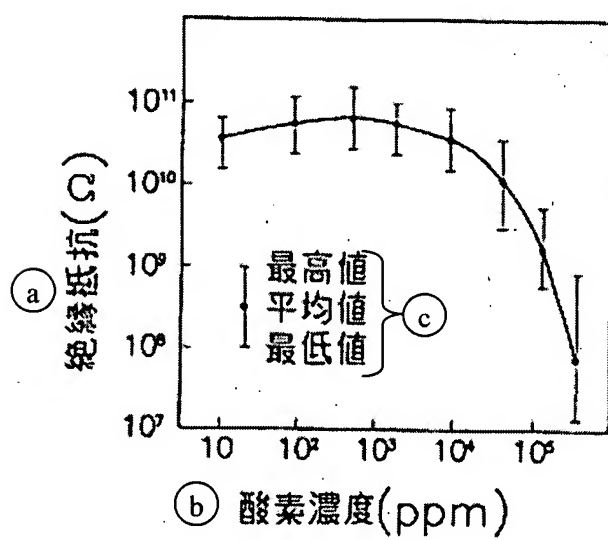


Figure 2

Key: a Insulation resistance (Ω)

b Oxygen density (ppm)

c Maximum value

Average value

Minimum value